

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 1 249 452 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

16.10.2002 Bulletin 2002/42

(51) Int Cl.7: C07D 487/04, A01N 43/90

(21) Application number: 01108841.6

(22) Date of filing: 09.04.2001

(84) Designated Contracting States:

AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE TR

Designated Extension States:

AL LT LV MK RO SI

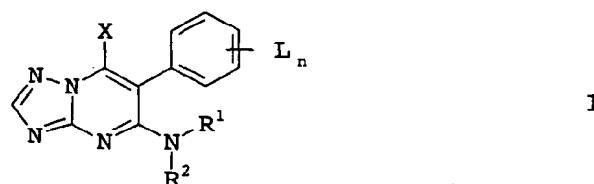
(71) Applicant: BASF AKTIENGESELLSCHAFT
67056 Ludwigshafen (DE)

(72) Inventors:

- Tormo i Blasco, Jordi, Dr.
67117 Limburgerhof (DE)
- Ammermann, Eberhard, Dr.
64646 Heppenheim (DE)
- Pees, Klaus-Jürgen, Dr.
55192 Mainz (DE)
- Pfrengle, Waldemar, Dr.
55444 Selbersbach (DE)

(54) Fungicidal 5-Alkylamino-6-phenyl-7-halo-triazolopyrimidines

(57) 5-Alkylamino-6-phenyl-7-halo-triazolopyrimidines of formula I



in which

R¹ and R² independently denote hydrogen or alkyl, alkenyl, alkynyl, alkadienyl, or haloalkyl, cycloalkyl, bicycloalkyl, phenyl, naphthyl, or 5- or 6-membered heterocycl, containing one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom, or 5- or 6-membered heteroaryl, containing one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom, or where R¹ and R² radicals may be unsubstituted or substituted as defined in the description,

R¹ and R² together with the interjacent nitrogen atom represent a 5- or 6-membered heterocyclic ring, containing one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom, which may be substituted;

L is hydrogen, halogen, alkyl, alkoxy and haloalkyl;

n is an integer from 1 to 5; and

X is halogen;

processes for their preparation, compositions containing them and to their use for combating phytopathogenic fungi.

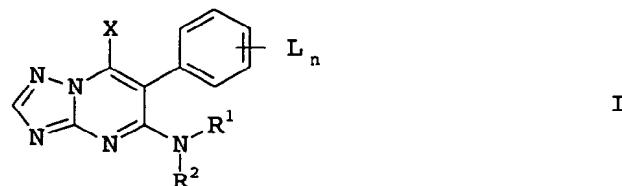
EP 1 249 452 A1

Description

[0001] The invention relates to 5-alkylamino-6-phenyl-7-halo-triazolopyrimidines of formula I

5

10



in which

15

R¹ and R² independently denote hydrogen or C₁-C₁₀-alkyl, C₂-C₁₀-alkenyl, C₂-C₁₀-alkynyl, C₄-C₁₀-alkadienyl, or C₁-C₁₀-haloalkyl, C₃-C₈-cycloalkyl, C₅-C₁₀-bicycloalkyl, phenyl, naphthyl, or 5- or 6-membered heterocyclyl, containing one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom, or 20 5- or 6-membered heteroaryl, containing one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom, or where R¹ and R² radicals may be unsubstituted or partially or fully halogenated or may carry one to three groups R^a,

25

R^a is halogen, cyano, nitro, hydroxyl, C₁-C₆-alkyl, C₁-C₆-haloalkyl, C₃-C₆-cycloalkyl, C₁-C₆-alkoxy, C₁-C₆-haloalkoxy, C₁-C₆-alkylthio, C₁-C₆-alkylamino, di-C₁-C₆-alkylamino, C₂-C₆-alkenyl, C₂-C₆-alkenyloxy, C₂-C₆-alkynyl, C₃-C₆-alkynyoxy and C₁-C₄-alkylenedioxy, which may be halogenated; or

30 R¹ and R² together with the interjacent nitrogen atom represent a 5- or 6-membered heterocyclic ring, containing one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom, which may be substituted by one to three R^a radicals;

35

L is hydrogen, halogen, C₁-C₁₀-alkyl, C₁-C₁₀-alkoxy and C₁-C₁₀-haloalkyl;

35 n is an integer from 1 to 5; and

X is halogen.

40 [0002] Moreover, the invention relates to processes for their preparation, compositions containing them and to their use for combating phytopathogenic fungi.

[0003] EP-A 071 792 discloses 6-phenyl-7-amino-triazolopyrimidines where the 5-position is substituted by hydrogen or alkyl or aryl groups.

[0004] EP-A 550 113 relates to 5-H- and 5-halogen-6-phenyl-7-amino-triazolopyrimidines where the 7-amino group is further substituted.

[0005] WO-A 98/46607 discloses fungicidal triazolopyrimidines, which are substituted in the 6-position by a 2,4,6-trifluorophenyl group.

[0006] The compounds disclosed in the documents discussed above are said to be active against various phytopathogenic fungi.

50 [0007] It is an object of the present invention to provide compounds having improved fungicidal activity.

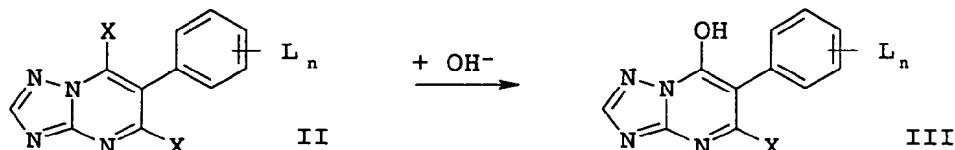
[0008] We have found that this object is achieved by the compounds defined at the outset. Furthermore, we have found processes for their preparation, compositions comprising them and methods for controlling phytopathogenic fungi using the compounds I.

[0009] The compounds of the formula I differ from the compounds known from the abovementioned art in the specific combination of the 5-alkylamino, 6-phenyl group and the halogen atom amino group in 5-position of the triazolopyrimidine system.

[0010] A 4- to 6-membered heterocyclic group may be any heterocyclic group with 4 to 6 ring atoms, interrupted by one or more heteroatoms selected from sulfur, nitrogen, and oxygen, preferably oxygen. A halogen atom suitable

denotes a fluorine, chlorine or bromine atom.

[0011] The present invention further provides a process for the preparation of compounds of formula I as defined above which comprises treating a 5,7-dihalo compound of formula II in which X is halogen with a hydroxide to 7-hydroxycompounds of formula III



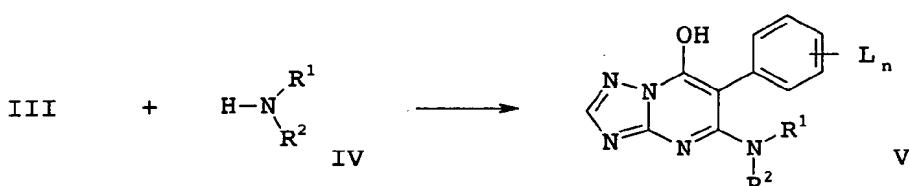
[0012] The reaction of compounds II with hydroxide is usually carried out in water and organic solvent at from 0°C to 80°C, preferably at from 20°C to 60°C.

[0013] Suitable solvents are ethers, such as tetrahydrofuran and alcohols. It is also possible to use mixtures of the solvents mentioned.

[0014] Suitable hydroxides are, in general, inorganic compounds, such as alkali metal and alkaline earth metal hydroxides (e.g. lithium hydroxide, sodium hydroxide, potassium hydroxide and calcium hydroxide).

[0015] It may be advantageous for the reaction to add a catalytic amount of a crown ether (e.g. 18-crown-6 or 15-crown-5).

[0016] The reaction can also be carried out in two-phase systems comprising a solution of alkali metal or alkaline earth metal hydroxides or carbonates in water and in organic phase (e.g. aromatic and/or halogenated hydrocarbons). Suitable phase transfer catalysts are, for example, ammonium halides and ammonium tetrafluoroborates (e.g. benzyltriethylammonium chloride, benzyltributylammonium bromide, tetrabutyl ammonium chloride, hexadecyl trimethyl ammonium bromide or tetrabutylammonium tetrafluoroborate) and phosphonium halides (e.g. tetrabutylphosphonium chloride and tetraphenylphosphonium bromide).

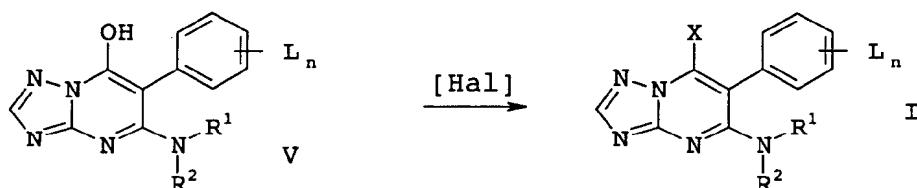


[0017] The reaction between the 5-halo-6-phenyl compound III and the amine of formula IV is preferably carried out in the presence of a solvent.

[0018] Suitable solvents include ethers, such as dioxane, diethyl ether and, especially, tetrahydrofuran, halogenated hydrocarbons such as dichloromethane and aromatic hydrocarbons, for example toluene.

[0019] The reaction is suitably carried out at a temperature in the range from 0°C to 70°C, the preferred reaction temperature being from 10°C to 35°C.

45 [0020] It is also preferred that the reaction is carried out in the presence of a base. Suitable bases include tertiary amines, such as triethylamine, and inorganic bases, such as potassium carbonate or sodium carbonate. Alternatively, an excess of the compound of formula V may serve as a base.



[0021] Compound of formula V is subsequently treated with a halogenating agent [Hall], preferably with a brominating agent [Hall].

or chlorinating agent, such as phosphorus oxybromide or phosphorus oxychloride, neat or in the presence of a solvent to give I.

[0022] The reaction is suitably carried out at a temperature in the range from 0 °C to 150 °C, the preferred reaction temperature being from 80 °C to 125 °C as disclosed for example by EP-A 770 615.

[0023] The reaction mixtures are worked up in a customary manner, for example by mixing with water, phase separation and, if required, chromatographic purification of the crude products. Some of the end products are obtained in the form of colorless or slightly brownish, viscous oils, which are purified or freed from volatile components under reduced pressure and at moderately elevated temperatures. If the end products are obtained as solids, purification can also be carried out by recrystallization or digestion.

[0024] Compounds of formula II are known in the art and can be obtained by synthesis routes disclosed in EP-A 550 113 and WO-A 98/46608.

[0025] If individual compounds I are not obtainable by the routes described above, they can be prepared by derivatization of other compounds I.

[0026] In the symbol definitions given in the formulae above, collective terms were used which generally represent the following substituents:

- halogen: fluorine, chlorine, bromine and iodine;
- C₁-C₁₀-alkyl and the alkyl moieties of C₁-C₁₀-haloalkyl: saturated, straight-chain or branched hydrocarbon radicals having 1 to 10, especially 1 to 6 carbon atoms, for example C₁-C₄-alkyl as mentioned above or pentyl, 1-methylbutyl, 2-methylbutyl, 3-methylbutyl, 2,2-di-methylpropyl, 1-ethylpropyl, hexyl, 1,1-dimethylpropyl, 1,2-dimethylpropyl, 1-methylpentyl, 2-methylpentyl, 3-methylpentyl, 4-methylpentyl, 1,1-dimethylbutyl, 1,2-dimethylbutyl, 1,3-dimethylbutyl, 2,2-dimethylbutyl, 2,3-dimethylbutyl, 3,3-dimethylbutyl, 1-ethylbutyl, 2-ethylbutyl, 1,1,2-trimethylpropyl, 1,2,2-trimethylpropyl, 1-ethyl-1-methylpropyl and 1-ethyl-2-methylpropyl;
- C₁-C₆-haloalkyl and the haloalkyl moieties of C₁-C₆-haloalkoxy: straight-chain or branched alkyl groups having 1 to 6, preferably 1 to 4 carbon atoms (as mentioned above), where the hydrogen atoms in these groups may be partially or fully replaced by halogen atoms as mentioned above, for example C₁-C₂-haloalkyl, such as chloromethyl, bromomethyl, dichloromethyl, trichloromethyl, fluoromethyl, difluoromethyl, trifluoromethyl, chlorofluoromethyl, dichlorofluoromethyl, chlorodifluoromethyl, 1-chloroethyl, 1-bromoethyl, 1-fluoroethyl, 2-fluoroethyl, 2,2-difluoroethyl, 2,2,2-trifluoroethyl, 2-chloro-2-fluoroethyl, 2-chloro-2,2-difluoroethyl, 2,2-dichloro-2-fluoroethyl, 2,2,2-trichloroethyl and pentafluoroethyl;
- C₃-C₁₀-alkenyl: unsaturated, straight-chain or branched hydrocarbon radicals having 3 to 10, especially 3 to 6 carbon atoms and a double bond in any position, for example 1-propenyl, 2-propenyl, 1-methylethenyl, 1-butenyl, 2-butenyl, 3-butenyl, 1-methyl-1-propenyl, 2-methyl-1-propenyl, 1-methyl-2-propenyl and 2-methyl-2-propenyl;

C₂-C₁₀-alkynyl: straight-chain or branched hydrocarbon radicals having 2 to 10, especially 2 to 4 carbon atoms and a triple bond in any position, for example ethynyl, 1-propynyl, 2-propynyl, 1-butynyl, 2-butynyl, 3-butynyl and 1-methyl-2-propynyl;

[0027] In general terms, the term cycloalkyl, as used herein with respect to a radical or moiety refers to a cycloalkyl group having 3 to 8 carbon atoms, preferably 5 to 7 carbon atoms.

[0028] In general terms, the term bicycloalkyl, as used herein with respect to a radical or moiety refers to a bicycloalkyl group having 5 to 10 carbon atoms, preferably 6 to 9 carbon atoms, in particular bicycloheptyl being optionally substituted by one or more halogen atoms, nitro, cyano, alkyl, preferably C₁-6 alkyl, alkoxy, preferably C₁-6 alkoxy.

[0029] 5-membered heteroaryl, containing one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom: 5-membered heteroaryl groups which, in addition to carbon atoms, may contain one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom as ring members, for example 2-furyl, 3-furyl, 2-thienyl, 3-thienyl, 2-pyrrolyl, 3-pyrrolyl, 3-isoxazolyl, 4-isoxazolyl, 5-isoxazolyl, 3-isothiazolyl, 4-isothiazolyl, 5-isothiazolyl, 3-pyrazolyl, 4-pyrazolyl, 5-pyrazolyl, 2-oxazolyl, 4-oxazolyl, 5-oxazolyl, 2-thiazolyl, 4-thiazolyl, 5-thiazolyl, 2-imidazolyl, 4-imidazolyl, 1,2,4-oxadiazol-3-yl, 1,2,4-oxadiazol-5-yl, 1,2,4-thiadiazol-3-yl, 1,2,4-thiadiazol-5-yl, 1,2,4-triazol-3-yl, 1,3,4-oxadiazol-2-yl, 1,3,4-thiadiazol-2-yl and 1,3,4-triazol-2-yl;

[0030] 6-membered heteroaryl, containing one to four nitrogen atoms: 6-membered heteroaryl groups which, in addition to carbon atoms, may contain one to three or one to four nitrogen atoms as ring members, for example 2-pyridinyl, 3-pyridinyl, 4-pyridinyl, 3-pyridazinyl, 4-pyridazinyl, 2-pyrimidinyl, 4-pyrimidinyl, 5-pyrimidinyl, 2-pyrazinyl, 1,3,5-triazin-2-yl and 1,2,4-triazin-3-yl.

[0031] With respect to their intended use, preference is given to triazolopyrimidines of the formula I having the following substituents, where the preference is valid in each case on its own or in combination:

[0032] The particularly preferred embodiments of the intermediates with respect to the variables correspond to those of the radicals X, R¹ and R² of formula I.

[0033] A preferred alkyl moiety is an ethyl or especially a methyl group.

[0034] A preferred haloalkyl moiety is the 2,2,2-trifluoroethyl or 1,1,1-trifluoroprop-2-yl group;

5 [0035] A preferred alkenyl moiety is allyl or especially a 2-methylallyl group.

[0036] A preferred cycloalkyl moiety is cyclopentyl being optionally substituted by one or more halogen atoms, nitro, cyano, alkyl, preferably C₁-C₆ alkyl, alkoxy, preferably C₁-C₆ alkoxy.

[0037] A preferred heteroaryl moiety is pyridyl, pyrimidyl, pyrazolyl or thienyl.

10 [0038] Preference is given to compounds of formula I in which any alkyl or haloalkyl part of the groups R¹ or R², which may be straight chained or branched, contains up to 10 carbon atoms, preferably 1 to 9 carbon atoms, more preferably 2 to 6 carbon atoms, any alkenyl or alkynyl part of the substituents R¹ or R² contains up to 10 carbon atoms, preferably 2 to 9 carbon atoms, more preferably 3 to 6 carbon atoms, any cycloalkyl part of the substituents R¹ or R² contains from 3 to 10 carbon atoms, preferably from 3 to 8 carbon atoms, more preferably from 3 to 6 carbon atoms, and any bicycloalkyl part of the substituents R¹ or R² contains from 5 to 9 carbon atoms, preferably from 7 to 9 carbon atoms. Any alkyl, alkenyl or alkynyl group may be linear or branched.

[0039] Likewise, preference is given to compounds of formula I wherein R¹ is not hydrogen.

20 [0040] Compounds of formula I are preferred in which R¹ represents a straight-chained or branched C₁-C₁₀-alkyl, in particular a branched C₃-C₁₀-alkyl group, a C₃-C₈-cycloalkyl, a C₅-C₉-bicycloalkyl, a C₃-C₈-cycloalkyl-C₁-C₆-alkyl, C₁-C₁₀-alkoxy-C₁-C₆-alkyl, a C₁-C₁₀-haloalkyl or a phenyl group being optionally substituted by one to three halogen atoms or C₁-C₁₀-alkyl or C₁-C₁₀-alkoxy groups.

[0041] Particular preference is given to compounds I in which R² represents a hydrogen atom, a C₁-C₁₀-alkyl or a C₁-C₁₀-haloalkyl group, in particular a hydrogen atom.

[0042] Besides, particular preference is given to compounds I in which R² is hydrogen.

[0043] Moreover, particular preference is given to compounds I in which R² is methyl.

25 [0044] Furthermore, particular preference is given to compounds I in which R² is ethyl.

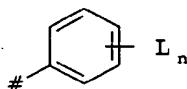
[0045] If R¹ denotes a C₁-C₁₀-haloalkyl group, preferably a polyfluorinated alkyl group, in particular a 2,2,2-trifluoroethyl, a 2-(1,1,1-trifluoropropyl) or a 2-(1,1,1-trifluorobutyl) group, R² preferably represents a hydrogen atom.

[0046] If R¹ denotes an optionally substituted C₃-C₈-cycloalkyl group, preferably a cyclopentyl or cyclohexyl group, R² preferably represents a hydrogen atom or C₁-C₆-alkyl group.

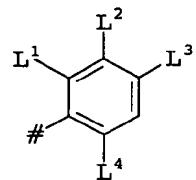
30 [0047] Moreover, particular preference is given to compounds I in which R¹ and R² together with the interjacent nitrogen atom form an optionally substituted heterocyclic ring, preferably an optionally substituted C₃-C₇-heterocyclic ring, in particular a pyrrolidine, piperidine, tetrahydropyridine, in particular 1,2,3,6-tetrahydropyridine or azepane ring which is optionally substituted by one or more C₁-C₁₀-alkyl groups.

[0048] L_n preferably is halogen or C₁-C₆-alkoxy. A preferred embodiment are compounds of formula I in which

35



represents



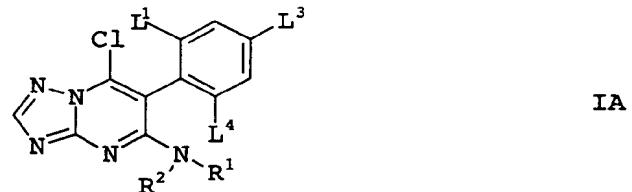
45 [0049] wherein # denotes the link to the triazolopyrimidine moiety, L¹ through L⁴ each independently represent hydrogen, especially fluorine, chlorine, methyl or methoxy, in particular wherein L¹ is fluoro, L² is hydrogen or fluoro, L³ is hydrogen or fluoro or methoxy and L⁴ denotes hydrogen, fluoro, chloro or methyl.

[0050] Moreover, particular preference is given to compounds of the formula I in which n is 2 or 3. Most preferred L⁴ is not hydrogen.

50 [0051] Furthermore, particular preference is given to compounds of formula IA in which the variables have the meaning as defined in formula I.

55

5



10 [0051] Preference is given to compounds of formula IA in which L¹ denotes halogen and L³ and L⁴ each independently represent hydrogen, halogen or C₁-C₄-alkoxy.

[0052] Most preferred are compounds of formula IA in which L¹ is fluoro, L³ is hydrogen and L⁴ is chloro.

[0053] Included in the scope of the present Invention are (R) and (S) isomers of compounds of general formula I having a chiral center and the racemates thereof, and salts, N-Oxides and acid addition compounds.

15 [0054] Particularly preference is given to compounds of formula IA wherein R² is hydrogen, L¹ and L⁴ independently represent fluorine or chlorine atoms, and L³ denotes hydrogen, fluorine, chlorine or methoxy.

[0055] Included in the scope of the present invention are (R) and (S) isomers of compounds of general formula I having a chiral center and the racemates thereof, and salts, N-oxides and acid addition compounds.

20 [0056] With respect to their use, particular preference is given to the compounds I compiled in the tables below. The groups mentioned in the table for a substituent are furthermore for their part, independently of the combination in which they are mentioned, a particularly preferred embodiment of the respective substituents.

Table 1

25 [0057] Compounds of the formula IA, in which L¹ is fluoro, L³ is hydrogen, L⁴ is chloro and R¹ and R² correspond to one row in Table A

Table 2

30 [0058] Compounds of the formula IA, in which L¹ and L⁴ each are fluoro, L³ is hydrogen and R¹ and R² correspond to one row in Table A

Table 3

35 [0059] Compounds of the formula IA, in which L¹ and L⁴ each are chloro, L³ is hydrogen and R¹ and R² correspond to one row in Table A

Table 4

40 [0060] Compounds of the formula IA, in which L¹ is methyl, L³ is hydrogen, L⁴ is fluoro and R¹ and R² correspond to one row in Table A

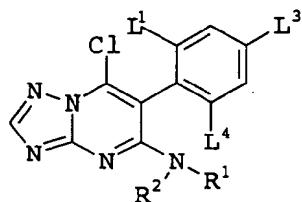
Table 5

45 [0061] Compounds of the formula IA, in which L¹, L³ and L⁴ each are fluoro and R¹ and R² correspond to one row in Table A

Table 6

50 [0062] Compounds of the formula IA, in which L¹ and L⁴ each are fluoro, L³ is methoxy and R¹ and R² correspond to one row in Table A

Table A



IA

No.	R ¹	R ²
A-1	CH ₂ CH ₃	H
A-2	CH ₂ CH ₃	CH ₃
A-3	CH ₂ CH ₃	CH ₂ CH ₃
A-4	CH ₂ CH ₂ CH ₃	H
A-5	CH ₂ CH ₂ CH ₃	CH ₃
A-6	CH ₂ CH ₂ CH ₃	CH ₂ CH ₃
A-7	CH ₂ CH ₂ CH ₃	CH ₂ CH ₂ CH ₃
A-8	CH ₂ CF ₃	H
A-9	CH ₂ CF ₃	CH ₃
A-10	CH ₂ CF ₃	CH ₂ CH ₃
A-11	CH ₂ CF ₃	CH ₂ CH ₂ CH ₃
A-12	CH ₂ CCl ₃	H
A-13	CH ₂ CCl ₃	CH ₃
A-14	CH ₂ CCl ₃	CH ₂ CH ₃
A-15	CH ₂ CCl ₃	CH ₂ CH ₂ CH ₃
A-16	CH(CH ₃) ₂	H
A-17	CH(CH ₃) ₂	CH ₃
A-18	CH(CH ₃) ₂	CH ₂ CH ₃
A-19	CH(CH ₃) ₂	CH ₂ CH ₂ CH ₃
A-20	(±) CH(CH ₂ CH ₃)CH ₃	H
A-21	(±) CH(CH ₂ CH ₃)CH ₃	CH ₃
A-22	(±) CH(CH ₂ CH ₃)CH ₃	CH ₂ CH ₃
A-23	(R) CH(CH ₂ CH ₃)CH ₃	H
A-24	(R) CH(CH ₂ CH ₃)CH ₃	CH ₃
A-25	(R) CH(CH ₂ CH ₃)CH ₃	CH ₂ CH ₃
A-26	(S) CH(CH ₂ CH ₃)CH ₃	H

No.	R ¹	R ²
A-27	(S) CH(CH ₂ CH ₃)CH ₃	CH ₃
A-28	(S) CH(CH ₂ CH ₃)CH ₃	CH ₂ CH ₃
A-29	(±) CH(CH ₃)—CH(CH ₃) ₂	H
A-30	(±) CH(CH ₃)—CH(CH ₃) ₂	CH ₃
A-31	(±) CH(CH ₃)—CH(CH ₃) ₂	CH ₂ CH ₃
A-32	(R) CH(CH ₃)—CH(CH ₃) ₂	H
A-33	(R) CH(CH ₃)—CH(CH ₃) ₂	CH ₃
A-34	(R) CH(CH ₃)—CH(CH ₃) ₂	CH ₂ CH ₃
A-35	(S) CH(CH ₃)—CH(CH ₃) ₂	H
A-36	(S) CH(CH ₃)—CH(CH ₃) ₂	CH ₃
A-37	(S) CH(CH ₃)—CH(CH ₃) ₂	CH ₂ CH ₃
A-38	(±) CH(CH ₃)—C(CH ₃) ₃	H
A-39	(±) CH(CH ₃)—C(CH ₃) ₃	CH ₃
A-40	(±) CH(CH ₃)—C(CH ₃) ₃	CH ₂ CH ₃
A-41	(R) CH(CH ₃)—C(CH ₃) ₃	H
A-42	(R) CH(CH ₃)—C(CH ₃) ₃	CH ₃
A-43	(R) CH(CH ₃)—C(CH ₃) ₃	CH ₂ CH ₃
A-44	(S) CH(CH ₃)—C(CH ₃) ₃	H
A-45	(S) CH(CH ₃)—C(CH ₃) ₃	CH ₃
A-46	(S) CH(CH ₃)—C(CH ₃) ₃	CH ₂ CH ₃
A-47	(±) CH(CH ₃)—CF ₃	H
A-48	(±) CH(CH ₃)—CF ₃	CH ₃
A-49	(±) CH(CH ₃)—CF ₃	CH ₂ CH ₃
A-50	(R) CH(CH ₃)—CF ₃	H
A-51	(R) CH(CH ₃)—CF ₃	CH ₃
A-52	(R) CH(CH ₃)—CF ₃	CH ₂ CH ₃
A-53	(S) CH(CH ₃)—CF ₃	H
A-54	(S) CH(CH ₃)—CF ₃	CH ₃
A-55	(S) CH(CH ₃)—CF ₃	CH ₂ CH ₃
A-56	(±) CH(CH ₃)—CCl ₃	H
A-57	(±) CH(CH ₃)—CCl ₃	CH ₃
A-58	(±) CH(CH ₃)—CCl ₃	CH ₂ CH ₃
A-59	(R) CH(CH ₃)—CCl ₃	H
A-60	(R) CH(CH ₃)—CCl ₃	CH ₃
A-61	(R) CH(CH ₃)—CCl ₃	CH ₂ CH ₃
A-62	(S) CH(CH ₃)—CCl ₃	H
A-63	(S) CH(CH ₃)—CCl ₃	CH ₃
A-64	(S) CH(CH ₃)—CCl ₃	CH ₂ CH ₃
A-65	CH ₂ C(CH ₃)=CH ₂	H

No.	R ¹	R ²
5	A-66 $\text{CH}_2\text{C}(\text{CH}_3)=\text{CH}_2$	CH_3
	A-67 $\text{CH}_2\text{C}(\text{CH}_3)=\text{CH}_2$	CH_2CH_3
10	A-68 cyclopentyl	H
	A-69 cyclopentyl	CH_3
	A-70 cyclopentyl	CH_2CH_3
	A-71	$-(\text{CH}_2)_2\text{CH}(\text{CH}_3)(\text{CH}_2)_2-$

[0063] The compounds I are suitable as fungicides. They have outstanding activity against a broad spectrum of phytopathogenic fungi, in particular from the classes of the *Ascomycetes*, *Deuteromycetes*, *Phycomycetes* and *Basidiomycetes*. Some of them act systemically, and they can be employed in crop protection as foliar- and soil-acting fungicides.

[0064] They are especially important for controlling a large number of fungi on a variety of crop plants such as wheat, rye, barley, oats, rice, maize, grass, bananas, cotton, soya, coffee, sugar cane, grapevines, fruit species, ornamentals and vegetables such as cucumbers, beans, tomatoes, potatoes and cucurbits, and on the seeds of these plants.

[0065] Specifically, they are suitable for controlling the following plant diseases:

Alternaria species on vegetables and fruit,
 25 Botrytis cinerea (gray mold) on strawberries, vegetables, ornamentals and grapevines,
 Cercospora arachidicola on peanuts,
 Erysiphe cichoracearum and Sphaerotheca fuliginea on cucurbits,
 Erysiphe graminis (powdery mildew) on cereals,
 Fusarium and Verticillium species on various plants,
 Helminthosporium species on cereals,
 30 Mycosphaerella species on bananas and peanuts,
 Phytophthora infestans on potatoes and tomatoes,
 Plasmopara viticola on grapevines,
 Podosphaera leucotricha on apples,
 Pseudocercospora herpotrichoides on wheat and barley,
 35 Pseudoperonospora species on hops and cucumbers,
 Puccinia species on cereals,
 Pyricularia oryzae on rice,
 Rhizoctonia species on cotton, rice and lawns,
 Septoria nodorum on wheat,
 40 Uncinula necator on grapevines,
 Ustilago species on cereals and sugar cane, and
 Venturia species (scab) on apples and pears.

[0066] Moreover, the compounds I are suitable for controlling harmful fungi such as *Paecilomyces variotii* in the protection of materials (e.g. wood, paper, paint dispersions, fibers and tissues) and in the protection of stored products.

[0067] The compounds I are applied by treating the fungi, or the plants, seeds, materials or the soil to be protected against fungal infection, with a fungicidally active amount of the active ingredients. Application can be effected both before and after infection of the materials, plants or seeds by the fungi.

[0068] In general, the fungicidal compositions comprise from 0.1 to 95, preferably 0.5 to 90, % by weight of active ingredient.

[0069] When used in crop protection, the rates of application are from 0.01 to 2.0 kg of active ingredient per ha, depending on the nature of the effect desired.

[0070] In the treatment of seed, amounts of active ingredient of from 0.001 to 0.1 g, preferably 0.01 to 0.05 g, are generally required per kilogram of seed.

[0071] When used in the protection of materials or stored products, the rate of application of active ingredient depends on the nature of the field of application and on the effect desired. Rates of application conventionally used in the protection of materials are, for example, from 0.001 g to 2 kg, preferably 0.005 g to 1 kg, of active ingredient per cubic meter of material treated.

[0072] The compounds I can be converted into the customary formulations, e.g. solutions, emulsions, suspensions, dusts, powders, pastes and granules. The use form depends on the particular purpose; in any case, it should guarantee a fine and uniform distribution of the compound according to the invention.

[0073] The formulations are prepared in a known manner, e.g. by extending the active ingredient with solvents and/or carriers, if desired using emulsifiers and dispersants, it also being possible to use other organic solvents as auxiliary solvents if water is used as the diluent. Auxiliaries which are suitable are essentially: solvents such as aromatics (e.g. xylene), chlorinated aromatics (e.g. chlorobenzenes), paraffins (e.g. mineral oil fractions), alcohols (e.g. methanol, butanol), ketones (e.g. cyclohexanone), amines (e.g. ethanolamine, dimethylformamide) and water; carriers such as ground natural minerals (e.g. kaolins, clays, talc, chalk) and ground synthetic minerals (e.g. highly-disperse silica, silicates); emulsifiers such as non-ionic and anionic emulsifiers (e.g. polyoxyethylene fatty alcohol ethers, alkylsulfonates and arylsulfonates) and dispersants such as lignin-sulfite waste liquors and methylcellulose.

[0074] Suitable surfactants are alkali metal, alkaline earth metal and ammonium salts of lignosulfonic acid, naphthalenesulfonic acid, phenolsulfonic acid, dibutylnaphthalenesulfonic acid, alkylarylsulfonates, alkyl sulfates, alkylsulfonates, fatty alcohol sulfates and fatty acids and their alkali metal and alkaline earth metal salts, salts of sulfated fatty alcohol glycol ether, condensates of sulfonated naphthalene and naphthalene derivatives with formaldehyde, condensates of naphthalene or of naphthalenesulfonic acid with phenol or formaldehyde, polyoxyethylene octylphenyl ether, ethoxylated isoocetylphenol, octylphenol, nonylphenol, alkylphenol polyglycol ethers, tributylphenyl polyglycol ethers, alkylaryl polyether alcohols, isotridecyl alcohol, fatty alcohol/ethylene oxide condensates, ethoxylated castor oil, polyoxyethylene alkyl ethers, ethoxylated polyoxypropylene, lauryl alcohol polyglycol ether acetal, sorbitol esters, lignin-sulfite waste liquors and methylcellulose.

[0075] Substances which are suitable for the preparation of directly sprayable solutions, emulsions, pastes or oil dispersions are mineral oil fractions of medium to high boiling point, such as kerosene or diesel oil, furthermore coal tar oils and oils of vegetable or animal origin, aliphatic, cyclic and aromatic hydrocarbons, e.g. benzene, toluene, xylene, paraffin, tetrahydronaphthalene, alkylated naphthalenes or their derivatives, methanol, ethanol, propanol, butanol, chloroform, carbon tetrachloride, cyclohexanol, cyclohexanone, chlorobenzene, isophorone, strongly polar solvents, e.g. dimethylformamide, dimethyl sulfoxide, N-methylpyrrolidone and water.

[0076] Powders, materials for scattering and dusts can be prepared by mixing or concomitantly grinding the active substances with a solid carrier.

[0077] Granules, e.g. coated granules, impregnated granules and homogeneous granules, can be prepared by binding the active ingredients to solid carriers. Examples of solid carriers are mineral earths, such as silicas, silica gels, silicates, talc, kaolin, attaclay, limestone, lime, chalk, bole, loess, clay, dolomite, diatomaceous earth, calcium sulfate, magnesium sulfate, magnesium oxide, ground synthetic materials, fertilizers, e.g. ammonium sulfate, ammonium phosphate, ammonium nitrate, ureas, and products of vegetable origin, such as cereal meal, tree bark meal, wood meal and nutshell meal, cellulose powders and other solid carriers.

[0078] In general, the formulations comprise of from 0.01 to 95% by weight, preferably from 0.1 to 90% by weight, of the active ingredient. The active ingredients are employed in a purity of from 90% to 100%, preferably 95% to 100% (according to NMR spectrum).

[0079] The following are exemplary formulations:

I. 5 parts by weight of a compound according to the invention are mixed intimately with 95 parts by weight of finely divided kaolin. This gives a dust which comprises 5% by weight of the active ingredient.

II. 30 parts by weight of a compound according to the invention are mixed intimately with a mixture of 92 parts by weight of pulverulent silica gel and 8 parts by weight of paraffin oil which had been sprayed onto the surface of this silica gel. This gives a formulation of the active ingredient with good adhesion properties (comprises 23% by weight of active ingredient).

III. 10 parts by weight of a compound according to the invention are dissolved in a mixture composed of 90 parts by weight of xylene, 6 parts by weight of the adduct of 8 to 10 mol of ethylene oxide and 1 mol of oleic acid N-monoethanolamide, 2 parts by weight of calcium dodecylbenzenesulfonate and 2 parts by weight of the adduct of 40 mol of ethylene oxide and 1 mol of castor oil (comprises 9% by weight of active ingredient).

IV. 20 parts by weight of a compound according to the invention are dissolved in a mixture composed of 60 parts by weight of cyclohexanone, 30 parts by weight of isobutanol, 5 parts by weight of the adduct of 7 mol of ethylene oxide and 1 mol of isoocetylphenol and 5 parts by weight of the adduct of 40 mol of ethylene oxide and 1 mol of castor oil (comprises 16% by weight of active ingredient).

V. 80 parts by weight of a compound according to the invention are mixed thoroughly with 3 parts by weight of

sodium diisobutylnaphthalene-alpha-sulfonate, 10 parts by weight of the sodium salt of a lignosulfonic acid from a sulfite waste liquor and 7 parts by weight of pulverulent silica gel, and the mixture is ground in a hammer mill (comprises 80% by weight of active ingredient).

5 VI. 90 parts by weight of a compound according to the invention are mixed with 10 parts by weight of N-methyl- α -pyrrolidone, which gives a solution which is suitable for use in the form of microdrops (comprises 90% by weight of active ingredient).

10 VII. 20 parts by weight of a compound according to the invention are dissolved in a mixture composed of 40 parts by weight of cyclohexanone, 30 parts by weight of isobutanol, 20 parts by weight of the adduct of 7 mol of ethylene oxide and 1 mol of isoctylphenol and 10 parts by weight of the adduct of 40 mol of ethylene oxide and 1 mol of castor oil. Pouring the solution into 100,000 parts by weight of water and finely distributing it therein gives an aqueous dispersion which comprises 0.02% by weight of the active ingredient.

15 VIII. 20 parts by weight of a compound according to the invention are mixed thoroughly with 3 parts by weight of sodium diisobutylnaphthalene- α -sulfonate, 17 parts by weight of the sodium salt of a lignosulfonic acid from a sulfite waste liquor and 60 parts by weight of pulverulent silica gel, and the mixture is ground in a hammer mill. Finely distributing the mixture in 20,000 parts by weight of water gives a spray mixture which comprises 0.1% by weight of the active ingredient.

20 [0080] The active ingredients can be used as such, in the form of their formulations or the use forms prepared therefrom, e.g. in the form of directly sprayable solutions, powders, suspensions or dispersions, emulsions, oil dispersions, pastes, dusts, materials for spreading, or granules, by means of spraying, atomizing, dusting, scattering or pouring. The use forms depend entirely on the intended purposes; in any case, this is intended to guarantee the finest possible distribution of the active ingredients according to the invention.

25 [0081] Aqueous use forms can be prepared from emulsion concentrates, pastes or wettable powders (sprayable powders, oil dispersions) by adding water. To prepare emulsions, pastes or oil dispersions, the substances as such or dissolved in an oil or solvent, can be homogenized in water by means of wetter, tackifier, dispersant or emulsifier. Alternatively, it is possible to prepare concentrates composed of active substance, wetter, tackifier, dispersant or emulsifier and, if appropriate, solvent or oil, and such concentrates are suitable for dilution with water.

30 [0082] The active ingredient concentrations in the ready-to-use products can be varied within substantial ranges. In general, they are from 0.0001 to 10%, preferably from 0.01 to 1%.

[0083] The active ingredients may also be used successfully in the ultra-low-volume process (ULV), it being possible to apply formulations comprising over 95% by weight of active ingredient, or even the active ingredient without additives.

35 [0084] Various types of oils, herbicides, fungicides, other pesticides, or bactericides may be added to the active ingredients, if appropriate also only immediately prior to use (tank mix). These agents can be admixed with the agents according to the invention in a weight ratio of 1:10 to 10:1.

40 [0085] In the use form as fungicides, the compositions according to the invention can also be present together with other active ingredients, e.g. with herbicides, insecticides, growth regulators, fungicides or else with fertilizers. Mixing the compounds I or the compositions comprising them in the use form as fungicides with other fungicides frequently results in a broader fungicidal spectrum of action.

45 [0086] The following list of fungicides, together with which the compounds according to the invention can be used, is intended to illustrate the possible combinations, but not to impose any limitation:

45 sulfur, dithiocarbamates and their derivatives, such as iron(III) dimethyldithiocarbamate, zinc dimethyldithiocarbamate, zinc ethylenebisdithiocarbamate, manganese ethylenebisdithiocarbamate, manganese zinc ethylenediaminebisdithiocarbamate, tetramethylthiuram disulfide, ammonia complex of zinc (N,N-ethylenebisdithiocarbamate), ammonia complex of zinc (N,N'-propylenebisdithiocarbamate), zinc (N,N'-propylenebisdithiocarbamate), N,N'-polypropylenebis(thiocarbamoyl)disulfide;

50 nitro derivatives, such as dinitro(1-methylheptyl)phenyl crotonate, 2-sec-butyl-4,6-dinitrophenyl 3,3-dimethylacrylate, 2-sec-butyl-4,6-dinitrophenylisopropyl carbonate, diisopropyl 5-nitro-isophthalate; heterocyclic substances, such as 2-heptadecyl-2-imidazoline acetate, 2,4-dichloro-6-(o-chloroanilino)-s-triazine, O,O-diethyl phthalimidophosphonothioate, 5-amino-1-[bis(dimethylamino)phosphinyl]-3-phenyl-1,2,4-triazole, 2,3-dicyano-1,4-dithioanthraquinone, 2-thio-1,3-dithiolo[4,5-b]quinoxaline, methyl 1-(butylcarbamoyl)-2-benzimidazolecarbamate, 2-methoxycarbonylaminobenzimidazole, 2-(2-furyl)benzimidazole, 2-(4-thiazolyl)benzimidazole, N-(1,1,2,2-tetrachloroethylthio)tetrahydrophthalimide, N-trichloromethylthiotetrahydrophthalimide, N-trichloromethylthiophthalimide, N-dichlorofluoromethylthio-N',N'-dimethyl-N-phenylsulfo-diamide, 5-ethoxy-3-trichloromethyl-1,2,3-thiadiazole, 2-thiocyanatomethylthiobenzothiazole, 1,4-dichloro-2,5-dimethoxybenzene, 4-(2-chloro-

5 rophenylhydrazone)-3-methyl-5-isoxazolone, pyridine-2-thiol 1-oxide, 8-hydroxyquinoline or its copper salt, 2,3-dihydro-5-carboxanilido-6-methyl-1,4-oxathiine, 2,3-dihydro-5-carboxanilido-6-methyl-1,4-oxathiine 4,4-dioxide, 2-methyl-5,6-dihydro-4H-pyran-3-carboxanilide, 2-methylfuran-3-carboxanilide, 2,5-dimethylfuran-3-carboxanilide, 2,4,5-trimethylfuran-3-carboxanilide, N-cyclohexyl-2,5-dimethylfuran-3-carboxamide, N-cyclohexyl-N-methoxy-2,5-dimethylfuran-3-carboxamide, 2-methylbenzanilide, 2-iodobenzanilide, N-formyl-N-morpholine-2,2,2-trichloroethyl acetal, piperazine-1,4-diybis-1-(2,2,2-trichloroethyl)formamide, 1-(3,4-dichloroanilino)-1-formylamino-2,2,2-trichloroethane; 2,6-dimethyl-N-tridecylmorpholine or its salts, 2,6-dimethyl-N-cyclododecylmorpholine or its salts, N-[3-(p-tert-butylphenyl)-2-methylpropyl]-cis-2,6-dimethyl-morpholine, N-[3-(p-tert-butylphenyl)-2-methylpropyl]-piperidine, 1-[2-(2,4-dichlorophenyl)-4-ethyl-1,3-dioxolan-2-yl-ethyl]-1H-1,2,4-triazole, 1-[2-(2,4-dichlorophenyl)-4-n-propyl-1,3-dioxolan-2-yl-ethyl]-1H-1,2,4-triazole, N-(n-propyl)-N-(2,4,6-trichlorophenoxyethyl)-N'-imidazolyl-urea, 1-(4-chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-1-yl)-2-butanone, 1-(4-chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-1-yl)-2-butanone, (2RS,3RS)-1-[3-(2-chlorophenyl)-2-(4-fluorophenyl)-oxiran-2-ylmethyl]-1H-1,2,4-triazole, α -(2-chlorophenyl)- α -(4-chlorophenyl)-5-pyrimidinemethanol, 5-butyl-2-dimethylamino-4-hydroxy-6-methylpyrimidine, bis(p-chlorophenyl)-3-pyridinemethanol, 1,2-bis(3-ethoxycarbonyl-2-thioureido)benzene, 1,2-bis(3-methoxycarbonyl-2-thioureido)benzene, strobilurines such as azoxystrobin, kresoxim methyl, methyl E-methoxyimino-[α -(2-phenoxyphenyl)]-acetamide, methyl E-methoxyimino-[α -(2,5-dimethylphenoxy)-o-tolyl]acetamide, picoxystrobin, pyraclostrobin, trifloxystrobin, anilinopyrimidines such as N-(4,6-dimethylpyrimidin-2-yl)aniline, N-[4-methyl-6-(1-propynyl)pyrimidin-2-yl]-aniline, N-[4-methyl-6-cyclopropylpyrimidin-2-yl]aniline, phenylpyrroles such as 4-(2,2-difluoro-1,3-benzodioxol-4-yl)pyrrole-3-carbonitrile, cinnamamides such as 3-(4-chlorophenyl)-3-(3,4-dimethoxyphenyl)acryloylmorpholine, and a variety of fungicides such as dodecylguanidine acetate, 3-[3-(3,5-dimethyl-2-oxycyclohexyl)-2-hydroxyethyl]glutarimide, hexachlorobenzene, methylN-(2,6-dimethylphenyl)-N-(2-furoyl)-DL-alaninate, DL-N-(2,6-dimethylphenyl)-N-(2'-methoxyacetyl)-alanine methyl ester, N-(2,6-dimethylphenyl)-N-chloroacetyl-D,L-2-amino- butyrolactone, DL-N-(2,6-dimethylphenyl)-N-(phenylacetyl)alanine methyl ester, 5-methyl-5-vinyl-3-(3,5-dichlorophenyl)-2,4-dioxa-1,3-oxazolidine, 3-[3,5-dichlorophenyl(5-methyl-5-methoxymethyl)-1,3-oxazolidine-2,4-dione, 3-(3,5-dichlorophenyl)-1-isopropylcarbamoylhydantoin, N-(3,5-dichlorophenyl)-1,2-dimethylcyclopropane-1,2-dicarboximide, 2-cyano-[N-(ethylaminocarbonyl)-2-methoximino]acetamide, 1-[2-(2,4-dichloro-phenyl)pentyl]-1H-1,2,4-triazole, 2,4-difluoro- α -(1H-1,2,4-triazolyl-1-methyl)benzhydryl alcohol, N-(3-chloro-2,6-dinitro-4-trifluoromethylphenyl)-5-trifluoromethyl-3-chloro-2-aminopyridine, 1-((bis(4-fluorophenyl)methylsilyl)methyl)-1H-1,2,4-triazole.

10

15

20

25

30

Synthesis Examples

[0087] With due modification of the starting compounds, the protocols shown in the synthesis examples below were used for obtaining further compounds I. The resulting compounds, together with physical data, are listed in the Table which follows.

Example 1: Preparation of 5-chloro-7-hydroxy-6-(2-chloro-6-fluorophenyl)-[1,2,4]-triazolo[1,5- α]pyrimidine

[0088] To a solution of 32 g (0.1 mol) 5,7-dichloro-6-(2-chloro-6-fluorophenyl)-[1,2,4]-triazolo[1,5- α]pyrimidine [cf. EP-A 550 113] in 200 ml tetrahydrofuran (THF) 50 ml of a 10% aq. solution of sodium hydroxide was added with stirring. After 1 h additional 25 ml sodium hydroxide solution are added and stirring was continued for 1 h after which no more starting material could be detected by TLC. After 16 ml conc. hydrochloric acid were added volatiles were distilled off. The product was extracted from the remainder with ethyl acetate. The two phase mixture was separated, the organic layer was dried. Adding light petroleum to the organic phase precipitated 22 g of the title compound as a tan powder of m.p. 257-259°C.

Example 2: Preparation of 5-(4-methylpiperid-1-yl)-7-hydroxy-6-(2-chloro-6-fluorophenyl)-[1,2,4]-triazolo[1,5- α]pyrimidine as 4-methylpiperidinium salt

[0089] 6.0 g (20 mmol) the compound from Example 1 and 12.0 g (120 mmol) 4-methylpiperidin were mixed and heated to 130°C for 4 days. After cooling to 50 to 60°C ethyl acetate was added and the precipitate formed was filtered off. 6.9 g of title compound were obtained after washing with ethyl acetate and drying.

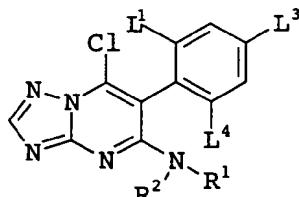
55 Example 3: Preparation of 5-(4-methylpiperid-1-yl)-7-chloro-6-(2-chloro-6-fluorophenyl)-[1,2,4]-triazolo[1,5- α]pyrimidine

[0090] A mixture of 3.6 g (7.5 mmol) Example 2 product and 15 ml phosphorous oxychloride was heated to 100°C

for 4 hours. After cooling the reaction mixture was poured onto a mixture of ice and sodium carbonate. Extraction with toluene and chromatography on silica gel (toluene/ethyl acetate mixtures 5:1 to 2:1) yielded 2.9 g of the title compound of m.p. 137-140°C.

5

Table I



IA

10

15

20

25

30

No.	R ¹	R ²	L ¹	L ³	L ⁴	phys. data (m.p. [°C])
I-1	CH(CH ₃) ₂	H	F	H	Cl	77
I-2	CH(CH ₃) ₂	H	F	H	F	159
I-3	CH(CH ₃) ₂	H	F	F	F	203
I-4	-(CH ₂) ₂ CH(CH ₃)(CH ₂) ₂ -		F	H	Cl	138
I-5	-(CH ₂) ₂ CH(CH ₃)(CH ₂) ₂ -		F	F	F	79
I-6	CH ₂ CH ₃	CH ₂ CH ₃	F	H	Cl	foam
I-7	(S) CH(CH ₃)-CF ₃	H	F	H	F	208
I-8	(S) CH(CH ₃)-CF ₃	H	F	F	F	218

Examples of the action against harmful fungi

[0091] The fungicidal action of the compounds of the formula I was demonstrated by the following experiments:
 [0092] The active compounds, separately or together, were formulated as a 10% emulsion in a mixture of 70% by weight of cyclohexanone, 20% by weight of Nekanil® LN (Lutensol® AP6, wetting agent having emulsifying and dispersant action based on ethoxylated alkylphenols) and 10% by weight of Wettol® EM (nonionic emulsifier based on ethoxylated castor oil) and diluted with water to the desired concentration.

40

Use example 1: Fungicidal control of apple scab (*Venturia inequalis*)

[0093] Young apple seedlings of the cultivar "Common" were grown in pots to the 4 to 5 leaf stage. These plants were sprayed to run-off with an aqueous suspension, containing the concentration of active ingredient mentioned in the table below, prepared from a stock solution containing 5 % of the active ingredient, 94 % cyclohexanone and 1 % emulsifier (Tween 20). After the plants had dried (3-5h), they were inoculated with an aqueous spore suspension of *Venturia inequalis*. Then the trial plants were immediately transferred to a humid chamber with 22 to 24°C and a relative humidity close to 100 % and were cultivated there for 2 days. For a period of further 2 weeks a cultivation in a greenhouse followed at 21 to 23°C and a relative humidity about 95 %. Then the extent of fungal attack on the leaves was visually assessed as % diseased leaf area.

[0094] In this test, the plants which had been treated with 12.5 ppm of the compound I-4 showed an infection of 7%, whereas the untreated plants were infected to 80%.

Use example 2: Fungicidal control of early blight on tomatoes (*Alternaria solani*)

55

[0095] Young tomato seedlings of the cultivar "Pixie II" were grown in pots to the 2 to 4 leaf stage. These plants were sprayed to run-off with an aqueous suspension, containing the concentration of active ingredient mentioned in the table below, prepared from a stock solution containing 5 % of the active ingredient, 94 % cyclohexanone and 1 % emulsifier

(Tween 20).

[0096] After the plants had dried (3-5h), they were inoculated with an aqueous spore suspension of *Alternaria solani* containing 15×10^3 spores per ml. Then the trial plants were immediately transferred to a humid chamber with 22 to 24°C and a relative humidity close to 100 % for 36 h. For a period of further 2 to 3 days a cultivation in a greenhouse followed at 21 to 23°C and a relative humidity about 95 %. Then the extent of fungal attack on the leaves was visually assessed as % diseased leaf area.

[0097] In this test, the plants which had been treated with 50 ppm of the compound I-4 showed an infection of 3%, whereas the untreated plants were infected to 90%.

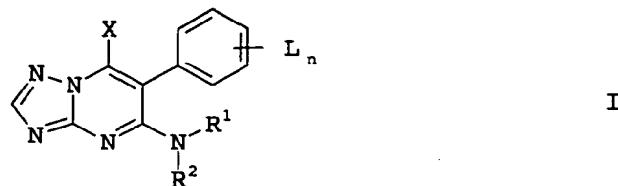
10 Use example 3: Fungicidal control of leaf spot on beets (*Cercospora beticola*)

[0098] Young sugar beet seedlings of the cultivar "ACH-31" were grown in pots to the 2 to 4 leaf stage. These plants were sprayed to run-off with an aqueous suspension, containing the concentration of active ingredient mentioned in the table below, prepared from a stock solution containing 5 % of the active ingredient, 94 % cyclohexanone and 1 % emulsifier (Tween 20). After the plants had dried (3-5h), they were inoculated with a spore suspension of *Cercospora beticola* in an aqueous solution of 0.5 % gelatine. Then the trial plants were immediately transferred to a humid chamber with 18 to 23°C and a relative humidity close to 100 % and kept there for 5 days. For a period of further 10 to 14 days a cultivation in a greenhouse followed at 21 to 23°C and a relative humidity about 95 %. Then the extent of fungal attack on the leaves was visually assessed as % diseased leaf area.

20 [0099] In this test, the plants which had been treated with 50 ppm of the compound I-4 showed an infection of 7%, whereas the untreated plants were infected to 70%.

Claims

25 1. 5-Alkylamino-6-phenyl-7-halo-triazolopyrimidines of formula I



35 in which

40 R¹ and R² independently denote hydrogen or C₁-C₁₀-alkyl, C₂-C₁₀-alkenyl, C₂-C₁₀-alkynyl, C₄-C₁₀-alkadienyl, or C₁-C₁₀-haloalkyl,

45 C₃-C₈-cycloalkyl, C₅-C₁₀-bicycloalkyl, phenyl, naphthyl, or 5- or 6-membered heterocyclyl, containing one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom, or

50 5- or 6-membered heteroaryl, containing one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom, or

55 where R¹ and R² radicals may be unsubstituted or partially or fully halogenated or may carry one to three groups R^a,

50 R^a is halogen, cyano, nitro, hydroxyl, C₁-C₆-alkyl, C₁-C₆-haloalkyl, C₃-C₆-cycloalkyl, C₁-C₆-alkoxy, C₁-C₆-haloalkoxy, C₁-C₆-alkylthio, C₁-C₆-alkylamino, di-C₁-C₆-alkylamino, C₂-C₆-alkenyl, C₂-C₆-alkenylloxy, C₂-C₆-alkynyl, C₃-C₆-alkynylloxy and C₁-C₄-alkylenedioxy, which may be halogenated; or

55 R¹ and R² together with the interjacent nitrogen atom represent a 5- or 6-membered heterocyclic ring, containing one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom, which may be substituted by one to three R^a radicals;

L is hydrogen, halogen, C₁-C₁₀ alkyl, C₁-C₁₀ alkoxy and C₁-C₁₀ haloalkyl;

5 n is an integer from 1 to 5; and

X is halogen.

10 2. Compounds of formula I according to claim 1, in which

R¹ is straight chained or branched C₁-C₆-alkyl, C₁-C₆-haloalkyl, straight chained or branched C₂-C₆-alkenyl, C₃-C₆-cycloalkyl, or C₅-C₉-bicycloalkyl, and

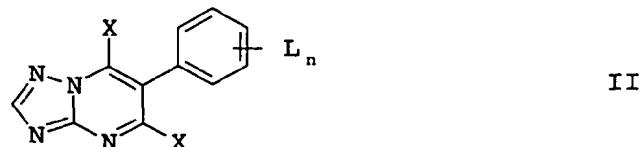
15 R² is hydrogen or C₁-C₆-alkyl, or

R¹ and R² together with the interjacent nitrogen atom represent a heterocyclic ring with 5 or 6 carbon atoms being optionally substituted with one or two C₁-C₆-alkyl groups;

20 15 L_n is 2-chloro-6-fluoro, 2,6-difluoro, 2,6-dichloro, 2-methyl-6-fluoro, 2,4,6-trifluoro, 2,6-difluoro-4-methoxy, or pentafluoro.

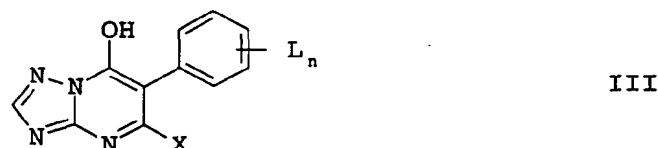
25 3. A process for the preparation of compounds of formula I as defined in claims 1 and 2 which comprises reacting 5,7-dihalo-6-phenyl-triazolopyrimidines of formula II

20



30 in which X is halogen with a base to 7-hydroxycompounds of formula III

30



40 in which X is halogen and after neutralisation reacting with an amine of formula IV

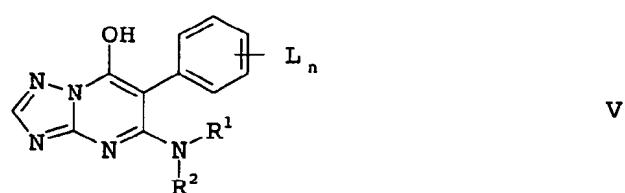
40



45

in which R¹ and R² are defined as in formula I to give 5-amino-7-hydroxycompounds of formula V

50



55

and further halogenation to produce compounds of formula I.

4. Compounds of formulae III and V as defined in claim 3.
5. A composition suitable for controlling phytopathogenic fungi, comprising a solid or liquid carrier and a compound of the formula I as claimed in claim 1.
- 5
6. A method for controlling phytopathogenic fungi, which comprises treating the fungi or the materials, plants, the soil or the seed to be protected against fungal attack with an effective amount of a compound of the formula I as claimed in claim 1.

10

15

20

25

30

35

40

45

50

55



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 01 10 8841

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
Y,D	EP 0 550 113 A (SHELL INT RESEARCH) 7 July 1993 (1993-07-07) * the whole document *	1-6	C07D487/04 A01N43/90
Y	WO 99 41255 A (AMERICAN CYANAMID CO) 19 August 1999 (1999-08-19) * the whole document *	1-6	
X	EP 0 782 997 A (SHELL INT RESEARCH) 9 July 1997 (1997-07-09)	3	
Y	* the whole document *	1-6	
Y	WO 94 20501 A (SHELL INT RESEARCH ;PEES KLAUS JUERGEN (DE); BECHER HEINZ MANFRED) 15 September 1994 (1994-09-15) * the whole document *	1-6	
Y,D	WO 98 46607 A (AMERICAN CYANAMID CO) 22 October 1998 (1998-10-22) * the whole document *	1-6	
Y,D	EP 0 071 792 A (BASF AG) 16 February 1983 (1983-02-16) * the whole document *	1-6	TECHNICAL FIELDS SEARCHED (Int.Cl.7) C07D
<p>The present search report has been drawn up for all claims</p>			
Place of search	Date of completion of the search	Exam. no.	
MUNICH	30 July 2001	STELLMACH, J	
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : Intermediate document			
T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.

EP 01 10 8841

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

30-07-2001

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
EP 0550113	A	07-07-1993		EP 0782997 A	09-07-1997
				GR 3033916 T	30-11-2000
				AT 159256 T	15-11-1997
				AT 192154 T	15-05-2000
				AU 667204 B	14-03-1996
				AU 3043592 A	01-07-1993
				BR 9205172 A	06-07-1993
				CA 2086404 A	01-07-1993
				CN 1075144 A, B	11-08-1993
				CN 1141119 A	29-01-1997
				DE 69222746 D	20-11-1997
				DE 69222746 T	12-02-1998
				DE 69230977 D	31-05-2000
				DE 69230977 T	09-11-2000
				DK 550113 T	09-02-1998
				DK 782997 T	07-08-2000
				ES 2108727 T	01-01-1998
				ES 2147411 T	01-09-2000
				GR 3025920 T	30-04-1998
				HK 1010105 A	23-06-2000
				HU 217349 B	28-01-2000
				IL 104244 A	13-07-1997
				JP 5271234 A	19-10-1993
				NZ 245581 A	26-07-1995
				PL 174047 B	30-06-1998
				PL 171579 B	30-05-1997
				PT 782997 T	29-09-2000
				RU 2089552 C	10-09-1997
				SG 47563 A	17-04-1998
				US 5593996 A	14-01-1997
				ZA 9210043 A	28-07-1993
WO 9941255	A	19-08-1999		US 6020338 A	01-02-2000
				AU 2595299 A	30-08-1999
				BR 9907863 A	24-10-2000
				CN 1292790 T	25-04-2001
				EP 1054888 A	29-11-2000
				HU 0100885 A	28-06-2001
EP 0782997	A	09-07-1997		EP 0550113 A	07-07-1993
				GR 3033916 T	30-11-2000
				AT 159256 T	15-11-1997
				AT 192154 T	15-05-2000
				AU 667204 B	14-03-1996
				AU 3043592 A	01-07-1993
				BR 9205172 A	06-07-1993

ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.

EP 01 10 8841

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

30-07-2001

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
EP 0782997	A			CA 2086404 A	01-07-1993
				CN 1075144 A, B	11-08-1993
				CN 1141119 A	29-01-1997
				DE 69222746 D	20-11-1997
				DE 69222746 T	12-02-1998
				DE 69230977 D	31-05-2000
				DE 69230977 T	09-11-2000
				DK 550113 T	09-02-1998
				DK 782997 T	07-08-2000
				ES 2108727 T	01-01-1998
				ES 2147411 T	01-09-2000
				GR 3025920 T	30-04-1998
				HK 1010105 A	23-06-2000
				HU 217349 B	28-01-2000
				IL 104244 A	13-07-1997
				JP 5271234 A	19-10-1993
				NZ 245581 A	26-07-1995
				PL 174047 B	30-06-1998
				PL 171579 B	30-05-1997
				PT 782997 T	29-09-2000
				RU 2089552 C	10-09-1997
				SG 47563 A	17-04-1998
				US 5593996 A	14-01-1997
				ZA 9210043 A	28-07-1993
WO 9420501	A	15-09-1994		AT 159722 T	15-11-1997
				AU 690899 B	07-05-1998
				AU 6258094 A	26-09-1994
				BR 9405988 A	26-12-1995
				CA 2157293 A	15-09-1994
				CN 1119015 A, B	20-03-1996
				CZ 9502233 A	17-01-1996
				DE 69406538 D	04-12-1997
				DK 699200 T	20-07-1998
				EP 0699200 A	06-03-1996
				HK 1004332 A	20-11-1998
				HU 73163 A	28-06-1996
				IL 108747 A	12-03-1999
				JP 8507505 T	13-08-1996
				NZ 262729 A	26-01-1996
				PL 310467 A	11-12-1995
				RU 2130459 C	20-05-1999
				SG 48860 A	18-05-1998
				SK 106895 A	05-06-1996
				US 5854252 A	29-12-1998
				ZA 9401485 A	10-11-1994

ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.

EP 01 10 8841

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

30-07-2001

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
WO 9846607	A	22-10-1998	AT AU EP	202779 T 6576898 A 0975634 A	15-07-2001 11-11-1998 02-02-2000
EP 0071792	A	16-02-1983	DE AT AU AU CA CS DD DE DK GR HU IE JP JP JP US ZA	3130633 A 11539 T 553663 B 8665982 A 1180329 A 226748 B 202093 A 3262143 D 341682 A, B, 76193 A 188325 B 53269 B 1634879 C 2061955 B 58043974 A 4567263 A 8205498 A	17-02-1983 15-02-1985 24-07-1986 10-02-1983 01-01-1985 16-04-1984 31-08-1983 14-03-1985 02-02-1983 03-08-1984 28-04-1986 28-09-1988 20-01-1992 21-12-1990 14-03-1983 28-01-1986 27-07-1983